

STUDY ON MICRO DROPLET REDUCTION ON TiN COATED BIOMEDICAL Ti-13Zr-13Nb ALLOY

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Abstract

Cathodic arc physical vapor deposition (CAPVD) is one of the physical Vapor deposition (PVD) techniques used to coat titanium nitride (TiN) on biomedical implants due to its good adhesion and high evaporation rate. However, this technique emits micro droplets which have can detrimental effect on the coating performance. Previous studies reported that micro droplets can be controlled through proper deposition parameters. In this paper, the PVD coating was performed on the Ti-13Zr-13Nb biomedical alloy with different substrate temperatures. Scanning electron microscopy (SEM) was used to characterized the surface morphology and coating thickness while X-Ray Diffraction (XRD) was employed to evaluate the crystal phase of the coated substrates. Image analysis software was used to quantify micro droplets counts. The results show that higher substrate temperature able to decrease a significant amount of micro droplets and concurrently increase the thickness of TiN coating. A mixed crystal planes of (111) and (200) are obtained on the coated substrates at this setting which exhibits denser structure as compared to substrates coated at lower substrate temperature.

Keywords: Microdroplets, CAPVD, Substrate temperature, TiN, Ti-13Zr-13Nb

Abstrak

Cathodic arc physical vapor deposition (CAPVD) merupakan salah satu teknik Physical vapor Deposition (PVD) yang digunakan untuk menyalut titanium nitrida (TiN) di implan bioperubatan disebabkan kekuatan lekatan yang baik dan kadar sejatan yang tinggi. Walau bagaimanapun, kaedah ini menghasilkan titisan mikro yang mempunyai kesan yang tidak baik ke atas salutan. Kajian lepas menunjukkan bahawa titisan mikro boleh dikawal melalui parameter salutan yang sesuai. Dalam kajian ini, salutan PVD telah dilakukan ke atas aloi bioperubatan Ti-13Zr-13Nb dengan suhu substrat yang berbeza. Mikroskop imbasan elektron (SEM) telah digunakan untuk menilai morfologi permukaan dan ketebalan lapisan manakala fasa kristal salut substrat telah diuji dengan menggunakan X-Ray Diffraction (XRD). Perisian analisis imej telah digunakan untuk mengukur bilangan dan saiz titisan mikro. Hasil kajian menunjukkan bahawa suhu substrat yang tinggi dapat mengurangkan sejumlah besar titisan mikro dan dapat meningkatkan ketebalan salutan TiN. Permukaan kristal campuran (111) dan (200) diperolehi pada salutan substrat yang dihasilkan pada aliran N₂ yang tinggi yang mana mempamerkan struktur yang padat dengan kekuatan lekatan yang lebih tinggi berbanding dengan substrat bersalut yang dihasilkan pada kadar aliran gas N₂ yang lebih rendah.

Kata kunci: Microdroplets, CAPVD, Suhu substrat, TiN, Ti-13Zr-13Nb

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1.0 INTRODUCTION

Titanium and its alloy are widely used for implant material for producing knee, shoulder, hip, plate support replacement. The titanium has advantages as compared with other conventional biomaterials (AISI 316L stainless steel, cobalt and chromium alloy) such as high strength to weight ratio, excellence corrosion resistance, superior biocompatibility and low elastic modulus [1-3]. Even the titanium has many advantages, this alloy is poor tribological properties when it contact or rubbing with other materials due to the relative motion in articulation joints would remove TiO protective layer and expose the bare material to corrosion attack. As a result of rubbing action, it would generate debris which causes toxic in the body environment [4]. This issue is a major concern in biomedical research thus lots of researchers try to reduce or eliminate completely this problem. It was reported that the surface modification method can increase resistance to corrosion and improves tribological behaviour. These techniques include Chemical Vapour Deposition (CVD) [5], Physical Vapour Deposition (PVD) [6], Ion Implantation [7] and Plasma Spray coating [8]. Among them, PVD is looked preferred choice because of its low processing temperature (<500 °C) over a wide range of coating thickness as compared to other methods. The problems exist in high processing temperature are detrimental effects on the physical and mechanical properties of the base material which restricts the type of substrates, unexpected phase transitions and excessive residual stresses due to the difference in thermal expansion between the deposited material and substrate [9]. Several types of PVD techniques are available such as Cathodic Arc Physical Vapour Deposition (CAPVD), magnetron sputtering, Electron beam physical vapour deposition, Evaporative deposition, and Pulsed laser deposition. Among PVD techniques, CAPVD offers better adhesion, high deposition rate, and low voltage power supply as compared to magnetron sputtering and vacuum deposition (evaporation) [10]. Despite these advantages, CAPVD emits micro droplets which have detrimental effect on the coating performance. It is well known that the micro droplets have poorly adhered on the substrate surface and their detachment causes pin holes defect [11]. This is considered as an undesirable phenomenon if occurs in coated biomedical implant where pin holes may act as channels for corrosion attack. Recently, TiN materials have been investigated widely as an effective coating material to enhance the performance of implants on account of their high hardness, wear resistance, and good corrosion, as well as good biocompatibility. Several studies have been conducted on TiN coating on the various substrates. For instance, Vadiraj and Kamaraj [12] compared the performance of TiN coating on fretting wear using plasma spray and PVD. They found that both methods improve the

fretting wear better than untreated samples. Subramanian *et al.* [13] studied the effect of the coated samples of TiN, Titanium Oxynitride (TiON) and Titanium Niobium Nitride (TiNbN) with untreated ones on cytotoxicity effect and platelet adhesion. They reported that coated samples improve platelet adhesion and become non-toxic when compared to untreated ones. Pham *et al.* [14] evaluated the effect of a TiN film on the mechanical properties and endothelial compatibility of a Co–Cr substrate. They noticed that TiN film able to improve the mechanical properties of the Co–Cr significantly and enhance the attachment and proliferation of endothelial cells on the coated substrate. Most of the previous studies focus on the improvement of TiN coating mechanical properties, cytotoxicity effect and cell attachment. Nevertheless, there is a limited report available in the literature addressing microdroplets issues when implant coated with TiN. It is believed that the presence of massive microdroplets on the coated substrate have a direct effect on the coating performance. Therefore, the aim of this study is to evaluate the effect of substrate temperature in reducing microdroplets deposits on Ti-13Zr-13Nb biomedical alloy during CAPVD coating.

2.0 METHODOLOGY

The material used in this study was Ti-13Zr-13Nb with the chemical compositions of the material in wt. %: are Nb: 14; Zr: 13.5; Fe: 0.05; C: 0.04; N: 0.02; H: 0.002; O: 0.10 and Ti: balance. The material was cut into diameter of 10mm x 2mm thick. First, the substrates were cleaned ultrasonically in acetone for 30 minutes, followed by a steam cleaning and then finally dried using a stream of compressed air. The substrates were ground with initial surface roughness, Ra of 0.1µm. CAPVD was employed to coat Ti-13Zr-13Nb alloy with TiN. Titanium of 99.99% purity was used as the target material. The substrates were etching with ion metal for 5 minutes at -1000V bias voltage for removing the oxide layer. Then the substrate was deposited under the following fixed parameters: cathodic current (100A), deposition time (1 hr), nitrogen gas flow rate (300 sccm (stands for standard cc per min), and substrate bias (-200V). The substrate temperature was varied from 100 to 300°C. The SEM was used to characterize the surface morphology and coating thickness. An XRD was used to determine the crystalline structure the TiN coating. The analysis of micro droplets deposits on the coated samples was performed using two different types of commercial image analyzer software.

3.0 RESULTS AND DISCUSSION

TiN coating was successfully deposited at different substrate temperature on the Ti-13Zr-13Nb alloy. The XRD results in Figure 1 illustrate the crystal planes of

the coated samples formed on the substrates at various substrate temperatures. The results confirm that TiN had different crystal planes ((111) and 200) on their substrates. The textured growth of the film with different planes improved the strength of the coated samples. Figure 1 shows the effect of substrate temperatures on the intensity plane of TiN coatings. As the substrate temperature increased from 100 to 300°C, the peak intensity of the (111) plane decreased whereas the intensity of the (2 0 0) plane increased regardless of N₂ flow rates. These results were in agreement with the results reported by Subramanian *et al.* [15]. The decreases experienced by crystal plane (111) were prominent at the substrate temperature of 300°C compared 100 °C. Increasing of PVD parameter from low to high polarity affected the kinetic energy of incident particles onto the substrate surface. The competition between the surface and strain energies in TiN film under these conditions affected the growth orientation.

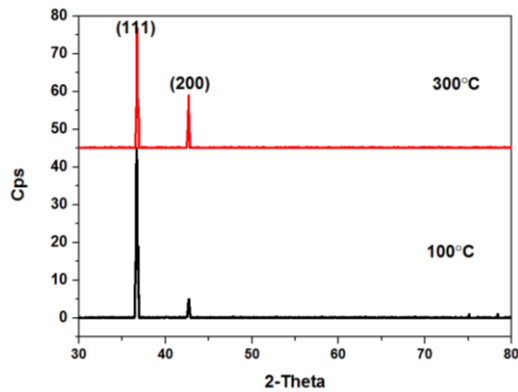
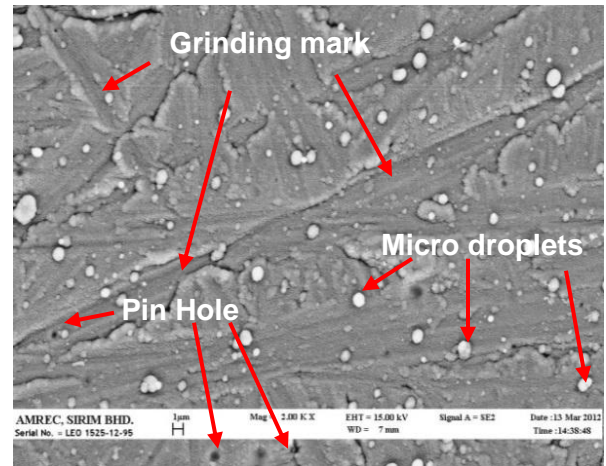
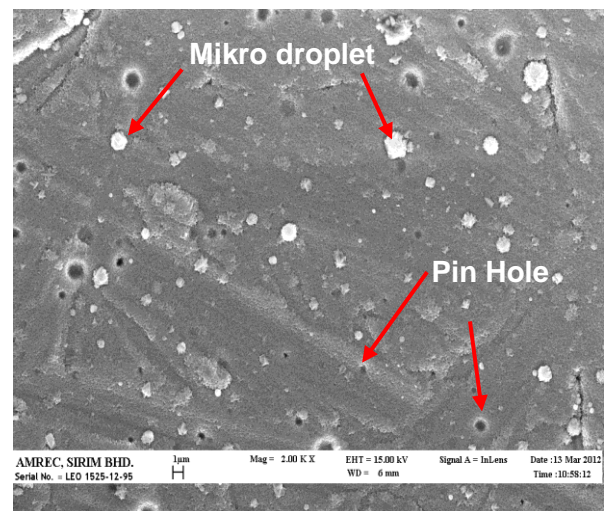


Figure 1. The XRD patterns of TiN coating deposited at different substrate temperature (a) 100°C (b) 300°C

The surface morphology results for TiN coated samples subjected to various substrate temperatures are shown in Figure 1. Distinct variations of TiN surface morphologies were observed on the coated samples at substrate temperatures of 100 °C and 300 °C. The micro droplets and pinholes were scattered across the TiN coated samples regardless of N₂ flow rates. Surface roughness with ploughing abrasive marks was still visible on the coated substrate for each coating conditions. It seems that the TiN coating at these parameters did not fill and cover the grinding marks. As substrate temperatures increased from 100 °C to 300 °C, the surface morphology of the coated samples became smooth. Similar features were observed by Mubarak *et al.*[16].



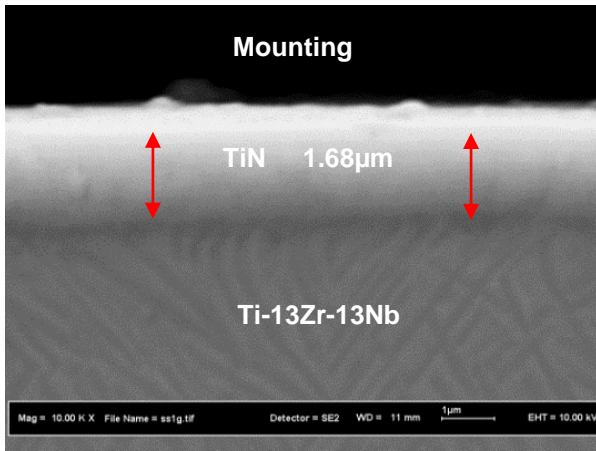
(a)



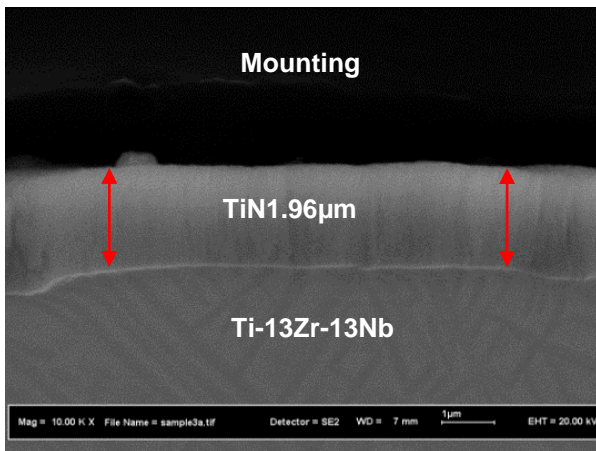
(b)

Figure 2 Surface morphology of TiN coated on Ti-13Zr-13Nb at different substrate temperature (a) 100°C (b) 300°C

Figure 3 shows a cross section that illustrates the effect of substrate temperatures on TiN coating thickness. The coatings were uniform, well adhered, and no void was presences in between the coating and the substrate. The cross sections are shown below confirm the results of the surface morphology analysis, which indicated that very thin coatings do not fill the grinding marks observed on the coating. The coating thickness increased as the substrate temperatures increased from 100 to 300°C regardless of N₂ flow rates as indicated in Figure 3. The substrate temperature had a significant effect on coating thickness.



(a)



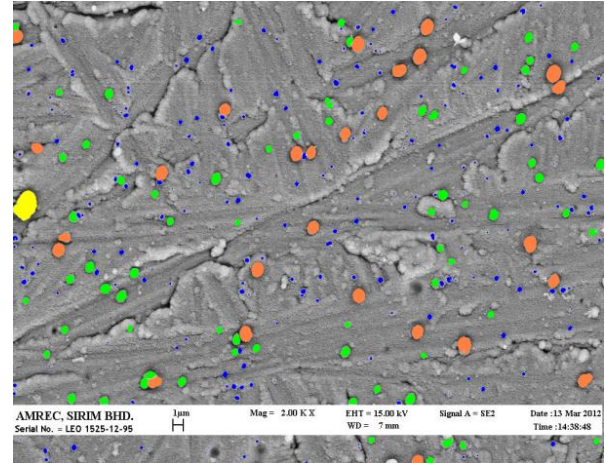
(b)

Figure.3 Cross sectional views of TiN coating thickness at different substrate temperature (a) 100°C(b) 300°C

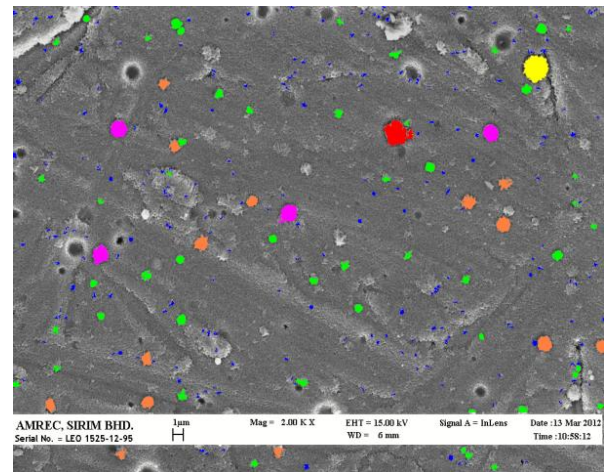
Image analysis software was used to verify the amount of micro droplets on the TiN coating surface. Prior to counting the micro droplets, the images in Figure 1 were enhanced using a sharpen edge filter and Photoshop software to improve for edge quality. This improved the contrast between the borders of the micro droplets and the TiN coating matrix. Second image analysis software was employed to quantify and classify micro droplets features into average ferret diameters and groups. This was completed by:

- i. Selecting the region of interest;
- ii. Image thresholding;
- iii. Image calibration;
- iv. Roundness adjustment; and
- v. The quantification and grouping of micro droplets according to their size.

In the final step, only micro droplets larger than 0.2 μm were grouped. Any micro droplets smaller than 0.2 μm were regarded as noise. The results of this analysis are shown in Figure 3. Well-defined micro droplets that fell within the acceptable range are represented using red and blue.



(a)



(b)

Figure 4 Output images of microdroplets counting using image analyzer at (a) 100°C (b) 300°C

Table 1 summarizes the counts in each range under different substrate temperatures. Specifically, substrates coated at 300°C have a lower micro droplets count compared to 100°C. This result proves that higher substrate temperatures able to reduce micro droplets deposition during coating.

Table 1 Summary Of Microdroplets Counts

Macrodroplets diameter, μm	Substrate Temperature	
	100°C	300°C
0.200 - 0.500	69	8
0.501 - 1.000	240	150
1.001 - 1.500	27	50
1.501 - 2.000	0	24
2.001 - 2.500	1	13
More	4	5
Total counts	341	250

4.0 CONCLUSION

TiN coating was successfully deposited on Ti-13Zr-13Nb alloy using CAPVD technique at two different substrate temperatures. The main results obtained from this study can be summarized as follows:

- i. Increasing substrate temperatures increased the coating thickness of the TiN coatings as well as decreased the number of micro droplets. Reduction in the microdroplets count on the coating surface has the potential to reduce the risk of corrosion attack when implants in the body fluid.
- ii. A dense, smooth and well adhered TiN coating without noticeable voids or cracks are successfully deposited on the Ti-13Zr-13Nb substrate. A higher substrate temperature provides higher coating thickness and vice versa.
- iii. XRD patterns show that a highly crystalline TiN phase ((111) and (200)) is feasible to be deposited on the Ti-13Zr-13Nb substrate within the range of studied coating parameters. Higher substrate temperature produces mixed crystal phases with dense coating structure.
- iv. The Initial surface roughness of the substrate has a direct influence on the smoothness of the TiN coating on the titanium-zirconium alloy. Surface finish of less than $0.1 \mu\text{m}$ is recommended for preparing titanium substrate for TiN deposition.

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References

- [1] Fukuda, A., Takemoto, M., Saito, T., Fujibayashi, S., Neo, M., Yamaguchi, S., Kizuki, T., Matsushita, T., Niinomi, M., Kokubo, T., And Nakamura, T. 2011. Bone Bonding

- Bioactivity Of Ti Metal And Ti-Zr-Nb-Ta Alloys With Ca Ions Incorporated On Their Surfaces By Simple Chemical And Heat Treatments. *Acta Biomaterialia*. 7(3): 1379-1386.
- [2] Kim, E. J., Jeong, Y. H., Choe, H. C., And Brantley, W.A. 2012. Surface Phenomena Of HA/Tin Coatings On The Nanotubular-Structured Beta Ti-29Nb-5Zr Alloy For Biomaterials. *Applied Surface Science*. 258(6): 2083-2087.
- [3] Rautray, T. R., Narayanan, R., and Kim, K. H. 2011. Ion Implantation Of Titanium Based Biomaterials. *Progress in Materials Science*. 56(8): 1137-1177.
- [4] Izman, S., Shah, A., Abdul-Kadir, M. R., Nazim, E. M., Anwar, M., Hassan, M.A., and Safari, H. 2012. Effect of Thermal Oxidation Temperature on Rutile Structure Formation of Biomedical TiZrNb Alloy. *Advanced Material Research*. 393-395: 704-708.
- [5] Bensheng, H., Ge, L., Zhongying, J., Wenfeng, Y., and Qi, X. 2015. Preparation and Characterization of Ceramic Film on Drilling Pipe Joint. *Rare Metal Materials and Engineering*. 44(6): 1357-1362.
- [6] Rahmati, B., Sarhan, A. A. D., Zalnezhad, E., Kamiab, Z., Dabbagh, A., Choudhury, D., and Abas, W. A. B. W. 2016. Development Of Tantalum Oxide (Ta-O) Thin Film Coating On Biomedical Ti-6Al-4V Alloy To Enhance Mechanical Properties And Biocompatibility. *Ceramics International*. 42(1, Part A): 466-480.
- [7] Sun, T., Xue, N., Liu, C., Wang, C., and He, J. 2015. Bioactive (Si, O, N)/(Ti, O, N)/Ti Composite Coating On NiTi Shape Memory Alloy For Enhanced Wear And Corrosion Performance. *Applied Surface Science*. 356: 599-609.
- [8] Dong, S., Song, B., Liao, H., and Coddet, C. 2015. Deposition Of NiCrBSi Coatings By Atmospheric Plasma Spraying And Dry-Ice Blasting: Microstructure And Wear Resistance. *Surface And Coatings Technology*. 268: 36-45.
- [9] Shah, A., Izman, S., Abdul-Kadir, M. R., Ayu, H. M., Anwar, M., and Ma'aram, A. 2014. Influence of Bias Voltage on Corrosion Resistance of TiN coated on Biomedical TiZrNb Alloy. *Advanced Materials Research*. 845: 436-440.
- [10] Liu, X., Chu, P. K., and Ding, C. 2004. Surface Modification Of Titanium, Titanium Alloys, And Related Materials For Biomedical Applications. *Materials Science And Engineering: R: Reports*. 47(3-4): 49-121.
- [11] Hosokawa, A., Shimamura, K., and Ueda, T. 2012. Cutting Characteristics Of PVD-Coated Tools Deposited By Unbalanced Magnetron Sputtering Method. *CIRP Annals - Manufacturing Technology*.
- [12] Vadiraj, A. and Kamaraj, M. 2007. Effect Of Surface Treatments On Fretting Fatigue Damage Of Biomedical Titanium Alloys. *Tribology International*. 40(1): 82-88.
- [13] Subramanian, B., Ananthakumar, R., and Jayachandran, M. 2011. Structural And Tribological Properties Of DC Reactive Magnetron Sputtered Titanium/Titanium Nitride (Ti/TiN) Multilayered Coatings. *Surface And Coatings Technology*. 205(11): 3485-3492.
- [14] Pham, V. H., Jun, S. H., Kim, H. E., and Koh, Y. H. 2012. Deposition Of Titanium Nitride (TiN) On Co-Cr And Their Potential Application As Vascular Stent. *Applied Surface Science*. 258(7): 2864-2868.
- [15] Subramanian, B., Ashok, K., and Jayachandran, M. 2008. Effect Of Substrate Temperature On The Structural Properties Of Magnetron Sputtered Titanium Nitride Thin Films With Brush Plated Nickel Interlayer On Mild Steel. *Applied Surface Science*. 255(5, Part 1): 2133-2138.
- [16] Mubarak, A., Hamzah, E., and Toff, M. R. M. 2008. Study Of Macrodroplet And Growth Mechanisms With And Without Ion Etchings On The Properties Of TiN Coatings Deposited On HSS Using Cathodic Arc Physical Vapour Deposition Technique. *Materials Science And Engineering: A*. 474(1-2): 236-242.